IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: :

    Wang et al.   :

Application No. 10/076,880   :   Art Unit: 1754

Filed: Feb. 13, 2002   :   Examiner: Edward Johnson

For: REFORMING CATALYTS AND   :   Atty Docket: 13199B
        METHODS OF ALCOHOL   :
        STEAM REFORMING   :

DECLARATION PURSUANT TO 37 CFR § 1.132

1.   We, the undersigned inventors, Yong Wang and Jianli Hu, are workers of at least ordinary skill in the field of catalysis.

2.   Attached to this Declaration is a 5 page document entitled "Comparison of MeOH Steam Reforming Catalyst with U.S. Patent 6,413,449." This document shows that the catalyst described in U.S. Patent No. 6,413,449, if tested according to conditions described in our specification (that is, at 300 °C and a mixture of water and methanol of 1.78, about 1 atm pressure and a contact time of 100 ms (or 150 ms)), would have a productivity that is substantially less than 10,000 ml H_2 / ml catalystAhr. The difference between our defined conditions of a water/methanol ratio of 1.78 and the

water/methanol ratio of 1.5 will not significantly affect the calculated result of volumetric productivity.

3.   Column 7, lines 13-17 in U.S. Patent No. 6,413,449 describe a part of a process of making a catalyst having the following steps "and is then reduced at constant temperature with an aqueous reducing agent, filtered, washed, dried, calcined in an oxidizing atmosphere at temperatures from 300°C to 550°C, and finally reduced in a hydrogen-containing gas at temperatures from 350°C to 500°C." A worker of ordinary skill in the field of making catalysts would not understand this part of the process as including any step of "depositing Pd." There is no scientific basis to believe that Pd is deposited during the steps desribed in this excerpt.

4.   A worker of ordinary skill in the field of making catalysts would not understand the descriptions of redispersing a catalyst powder and coating a carrier body at col. 7, lines 22-24 of U.S. Patent No. 6,413,449 to include any step of "depositing Pd."
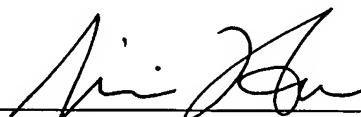
5.   Reforming methanol to produce hydrogen and reforming ethyl aromatics to produce methyl aromatics are totally different processes. In reforming ethyl aromatics to produce methyl aromatics, the scission of the C-C bond in the ethyl group is critical to forming methyl aromatics. In contrast, methanol does not have any C-C bonds. A worker of ordinary skill in the field of methanol steam reforming would know that the catalysts and mechanisms in converting ethyl aromatics to methyl aromatics are not relevant to the catalysts and mechanisms involved in methanol steam reforming.

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6. I declare that all of the above statements made of my own knowledge are true and all statements made on information and belief are believed to be true. I understand that willful false statements and the like are punishable by fine or imprisonment, or both (18 U.S.C. §1001), and may jeopardize the validity of the application or any patent issuing thereon.

Date: 12/10/2004   By: _____
                               Yong Wang

Date: 2-10-2004   By: _____
                               Jianli Hu

Comparison of MeOH Steam Reforming Catalyst with U.S. Patent 6,413,449

1. Analysis of Relevant Information from U.S. Patent 6,413,449

a) In Wieland's patent, conversion of MeOH is not given. They report catalyst performance based on CO_2 selectivity and hydrogen productivity. In the patent, CO_2 selectivity is defined as $S_{CO2}=P_{CO2}/(P_{CO2} + P_{CO})$, hydrogen productivity is defined as $P_{cat}=V_{H2}/M_{cat}.t[Nm^3/kg_{cat}.h]$.

b) Because of high CO_2 selectivity is obtained, steam reforming reaction is dominate:
$CH_3OH + H_2O \rightarrow 3 H_2 + CO_2$
This means, when 1 mol methanol is converted, 3 mol of hydrogen will be produced.

c) On page 8 of the patent, it is indicated that catalysts are all examined at LHSV=5 h^{-1} (total LHSV=8.3 h^{-1}) which is equivalent to 5 ml MeOH/ml catalyst. h. Based on this number, the maximum H_2 productivity per volume of catalyst per hour can be calculated as follow:

Maximum H_2 productivity=5 (ml MeOH/ml catalyst. h) x 0.791 (g/ml)/32 (g/mol) * 3 (mol H_2) * 22414 ml= 8310 ml/ml catalyst. h.

This is the H_2 productivity at 100% MeOH conversion

2. Performance Comparison

In order to make a fair comparison on catalyst performance, we should express hydrogen productivity on per catalyst volume basis (H_2/ml catalyst .h), not on weight basis. This is because the volume of catalyst is important in determining the efficiency of reformer. The productivity based on weight of catalyst or weight of Pd can only be used for kinetic study but may not precisely reflect efficiency of reformer, especially when catalysts of different density are compared. The following comparisons are made by assuming the best scenario for Wieland's patent.

From Wieland's Patent:

As shown in Table 1 of Example 1, on raising temperature from 300 to 400°C, the hydrogen productivity continues to increase. This implies that at 300°C, the conversion is not 100%. As a result, we can calculate the best scenario by assuming that 100% conversion is reached at 400°C. That means, at 300°C, only 57% MeOH conversion is obtained (37.8/66.2=57%, data from column 4 of Table 1).

Therefore, productivity of H_2 at 300°C= 0.57 * Maximum Productivity=4737 ml/ ml catalyst. h.

From Our Patent Application:

As shown in Attached Table, at 284°C and LHSV=30.5h^{-1}, methanol conversion of 99.9 % and hydrogen productivity of 29,000 ml/ ml catalyst. h are obtained, respectively. This clearly indicates that higher productivity achieved on our catalyst is not simply caused by operating at high throughput, otherwise we will not achieve 100% conversion. It is because the unique catalytic properties, allowing to operate at high turn over rate to achieve high productivity.

In fact, to compare our catalyst at 100% conversion with Wieland's at 57% conversion has put us in unfavorable conditions. The following is an exercise to compare our catalyst with the U.S. patent at the same methanol of conversion level of 57%. We know from Table 1 that, at 284°C and LHSV=30.5 h^{-1}, 99.9% conversion is achieved. By pushing the feed rate up (increase LHSV), conversion is going to decrease. The question is, at what LHSV, 57% conversion is going to be achieved. By assuming first order kinetics, which is commonly accepted for steam reforming reaction, we have calculated that feed rate should be increased to LHSV=249.6 h^{-1} in order to reach 57% conversion (See Appendix).

At LHSV=249.6 h^{-1}, and 57% conversion, hydrogen productivity is 131,400 ml/ml catalyst. h, this is even higher than what we reported at 100% conversion (29,000 ml/ml catalyst. h)

In conclusion, our powder catalyst is much more active than those mentioned in Wieland's patent.

Wieland's Catalyst Hydrogen Productivity at 150ms.

First we need to calculate WHSV$_{MeOH}$ at 150 ms, then use first order kinetics to calculate MeOH conversion at this contact time, and hydrogen productivity will be easy to calculate.

150ms is equivalent to total GHSV=24,000h^{-1}, which is total feed rate of 24,000 ml/ml catalyst.h.

This can be converted into total feed rate of 1.071 mol /ml catalyst. h .   (24000/22400).

Because H_2O/MeOH =1.5 (mol/mol), the above feed rate is equivalent to : (0.43 mol MeOH +0.641 mol H_2O)/ml cat. H.

So, at 150 ms, MeOH feed rate: WHSV$_{MeOH}$= 0.43 mol/ml cat.h=13.76 g/ml cat.h.

As discussed in the previous section, at 300°C, LHSV=5 h^{-1} (WHSV$_{MeOH}$=3.95 g/ ml cat.h), conversion of Wieland catalyst is 57%. Then, what is the conversion at WHSV$_{MeOH}$=13.76 g/ ml cat.h ?

Using the first order kinetics listed in Appendix, we obtained conversion=22%,
Therefore, hydrogen productivity at 150ms= 13.76/32 *0.22 x3 x22400=6360 ml/mlcat.h

*Wieland's Catalyst Hydrogen Productivity at **100ms**.*

Again, we need to calculate $WHSV_{MeOH}$ at 100 ms, then use first order kinetics to calculate MeOH conversion at this contact time, and hydrogen productivity will be easy to calculate.

150ms is equivalent to total $GHSV=36,000h^{-1}$, which is total feed rate of 36,000 ml/ml catalyst.h.

This can be converted into total feed rate of 1.607 mol /ml catalyst. h .   (36000/22400).

Because $H_2O/MeOH =1.5$ (mol/mol), the above feed rate is equivalent to : (0.643 mol MeOH +0.964 mol H_2O)/ml cat. h.

So, at 100 ms, MeOH feed rate: $WHSV_{MeOH}$= 0.643 mol/ml cat.h=20.58 g/ml cat.h.

As discussed in the previous section, at 300°C, LHSV=5 h^{-1} ($WHSV_{MeOH}$=3.95 g/ ml cat.h), conversion of Wieland catalyst is 57%. Then, what is the conversion at $WHSV_{MeOH}$=20.58 g/ ml cat.h ?

Using the first order kinetics listed in Appendix, we obtained conversion=15%,
Therefore, hydrogen productivity at 100ms= 20.58/32 *0.15 x3 x22400=6483 ml/mlcat.h

Table 1. Comparison of Velocys MeOH SR Catalyst with U.S. Patent 6,413,449

Characteristics and Performance	Velocys' SR Catalyst		U.S. Patent 6,413,449
	Engineer	Powder	
Composition of Active Component, wt%			
Al_2O_3	60-80	60-80	70-80
ZnO	10-30	10-30	10-20
Pd	10	10	1-5
Engineered Supports	FrCrAlY Felt	None	Ceramic Honeycomb
Method of Making Active component $Pd/ZnO/Al_2O_3$	Precipitation of Zn on Al_2O_3 then impregnate Pd. Wash-coat on felt	Precipitation of Zn on Al_2O_3 then impregnate Pd	Impregnate Zn and Pd simultaneously on Al_2O_3 coated on ceramic Honeycomb
Testing Conditions			
P, atm	1	1	1
T, °C	300	284	300
LHSV, h^{-1}	130	30.5	8.3 (5 for MeOH only)
Conversion of MeOH	82%	99.9%	57% (Assuming 100% conversion at 400°C)
Productivity, ml H_2/ml catalyst .h	90,000	29,000	4,737

Appendix

For first order plug flow reactor, the following kinetic equation will hold:

$$WHSV_{MeOH} = KC_{MeOH}M_{MeOH}/-Ln(1-X_{MeOH})---(1)$$

Where,
K=rate constant, function of temperature
C_{MeOH}=MeOH concentration at reactor inlet (mol/ml)
M_{MeOH}= Methanol molecular weight
$WHSV_{MeOH}$=weight hourly space velocity of methanol
X_{MeOH} =conversion of methanol

It is noted from equation (1) when temperature is not changed, $KC_{MeOH}M_{MeOH}$ remains constant. MeOH conversion X_{MeOH} should decrease with increase in $WHSV_{MeOH}$. Using this kinetic equation, by entering $WHSV_{MeOH}$ at 99.9% (13.4), we obtained $WHSV_{MeOH}$ at 57% conversion=109.7 h^{-1}, which is equivalent to LHSV=249.6 h^{-1} (S/C=1.78)

S/C=	1.78	w/w=	1.00125
LHSV=	30.5	Density=	0.88
Total WHSV=	26.84	g/cc.h	
WHSV MeOH=	13.41162	g/cc.h	
WHSV H2O	13.42838	g/cc.h	

Conversion at LHSV=30.5h-1	0.999	
Conversion at 57%	0.57	
Calculated WHSV MeOH at 57%	109.7719	g/cc.h
WHSV H2Oat 57%	109.9091	g/cc.h
Total LHSV	249.6374	h-1